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(54) **Curable acrylic polymer compositions and their preparation**

(57) A curable acrylic polymer composition useful in coating, sealant or adhesive compositions comprises an acrylic polymer containing pendant functional groups selected from epoxide groups, isocyanate groups, alkoxy silane groups and activated -CH- groups bonded to at least two electron-withdrawing groups and a curing agent which is reactive with the functional groups of the acrylic polymer and is characterised in that the polymer is dissolved in an organic compound of viscosity less than 2 Pas (20 poise) at 25°C containing at least one functional group of the same functionality as that present in the acrylic polymer. The composition can be prepared by the free radical polymerisation of a functional olefinically unsaturated monomer, and optionally one or more ethylenically unsaturated comonomers, in the presence of the said functional organic compound as diluent.

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Curable Polymer Compositions and their Preparation

This invention relates to curable polymer compositions such as coating, sealant or adhesive compositions and to their preparation.

5        There has been increased concern in recent years about the release of volatile solvents into the atmosphere, and there has been a consequent need to reduce the volatile organic solvent content of coating, sealant and adhesive compositions. This has not been easy for coating  
10 compositions, which require a relatively low viscosity of about 2-10 poise for application by the usual methods of spray, roller or brush, and particularly not for coating compositions which have to be applied and cure rapidly at ambient temperature, for example coatings for large  
15 structures such as ships, bridges, buildings, industrial plant and oil rigs. Coating compositions generally need to contain a polymer to confer film-forming properties, but any polymer needs to be of low molecular weight to give the required low viscosity, particularly after pigmentation as  
20 a paint. Preparation of low molecular weight acrylic polymers uses substantial quantities of polymerisation initiator and/or chain transfer agent and is highly exothermic, necessitating polymerisation in a solvent to control the exotherm. Preparation in a volatile organic  
25 solvent followed by stripping of the solvent is possible but is economically unattractive.

EP-A-206072 describes a semi-continuous process for preparing a polymeric reaction product which comprises the vinyl addition polymerisation of a vinyl monomer component  
30 selected from alkyl acrylates, alkyl methacrylates, monoalkenyl aromatic vinyl monomers, functional vinyl monomers and mixtures thereof at a temperature of at least 150°C in the presence of a diluent selected from polyester polyols, carboxyl-functional polyesters, polyester urethane  
35 polyols, polyester polyepoxides and polyether polyols and

having a molecular weight of at least 200, resulting in an ungelled product.

WO 90/03991 describes a method for producing a modified addition polymer from an ethylenically unsaturated monomer composition that includes at least one monomer having hydroxyl or carboxyl functionality, the method comprising polymerising said monomer composition by dissolving it and a free radical initiator therefor in a solvent-free molten composition maintained at a temperature supporting addition polymerisation of the monomer composition, the molten composition comprising a cyclic compound reactive via ring-opening with said hydroxyl or carboxyl functionality.

EP-A-433711 describes a terpolymer of a monovinyllic aromatic monomer, an acrylic monomer and maleic anhydride formed according to a polymerisation method in which the maleic anhydride is added to the reactor in a molten state, free of solvents and diluents, and the polymerisation reaction is conducted in bulk in the absence of solvents and diluents.

US-A-475112 describes a process for preparing a cured film coating comprising mixing until homogeneous a high-solids composition comprising a hydroxyl-functional acrylic polymer, an alkylolated melamine and a polycaprolactone polyol, applying the composition as a film coating on a surface, and curing the film coating by baking to crosslink the alkylolated melamine with the hydroxyl-functional acrylic polymer and the polycaprolactone polyol.

US-A-4556693 describes high-solids coating compositions containing a hydroxyl-functional acrylic copolymer-based resin and having higher total solids content and, when cured, with enhanced weathering resistance and hardness, characterised in that part of the acrylic base resin is replaced with a binary reactive diluent comprising a reactive acrylic oligomer of a hydroxyalkyl acrylate or methacrylate, an alkyl acrylate or methacrylate, and a

polycaprolactone hexol.

US-A-5004828 describes acrylic-modified hydroxy-functional polyester reactive diluents derived from triols and a combination of unsaturated monocarboxylic acids and 5 saturated monocarboxylic acids. These hydroxy-functional polyester diluents may be copolymerised with one or more hydroxy-functional acrylic monomers and blended with a variety of thermosetting or thermoplastic film-forming polymers.

10 A process according to the present invention for the preparation of a curable polymer composition by the free radical polymerisation of a functional olefinically unsaturated monomer, which contains a functional group which is capable of reacting with a curing agent, and optionally 15 one or more ethylenically unsaturated comonomers, is characterised in that the polymerisation is carried out in the presence of a reactive diluent which is a liquid organic compound of viscosity less than 20 poise at 25°C having at least one functional group which is substantially non- 20 reactive with the functional olefinically unsaturated monomer and which is capable of reacting with a curing agent to form a polymer network. By "viscosity" we mean the high-shear viscosity as determined by an I.C.I. cone and plate viscometer.

25 The process of the invention can be used to prepare a curable addition polymer composition of viscosity less than 50 poise, for example of viscosity 1 to 2 poise up to 30 or 40 poise. A polymer composition so prepared, when mixed with a curing agent which may be of lower viscosity, can form a 30 coating composition having a viscosity up to 10 poise, for example 2 to 6 poise, so that it can be applied to a substrate by conventional spray, roller or brush, without dilution by a volatile organic solvent. The use of volatile solvent can thereby be avoided both during preparation of 35 the curable addition polymer and during application of a coating or sealant or adhesive, or the amount of volatile

solvent can be reduced to a very low level such as less than 20% or even less than 10% by weight of the composition. If a low level of non-reactive volatile solvent is present during the polymerisation it may either be retained in the coating composition or be stripped from the composition after polymerisation is completed.

The functional group of the reactive diluent is preferably capable of reacting with the same curing agent with which the functional group of the olefinically unsaturated monomer reacts, so that the curable addition polymer and the reactive diluent can be linked by the curing agent in the same polymer network. Most preferably, the functional group of the reactive diluent has the same functionality as the functional monomer. The reactive diluent should be substantially non-reactive both with the functional group of the monomer and with the olefinic double bond of the monomer.

The functional olefinically unsaturated monomer is preferably an acrylic monomer, particularly an acrylic ester, such as an acrylate or methacrylate, substituted by a reactive functional group.

In most cases, at least some of the reactive diluent preferably contains at least two of the said functional groups, although reactive diluents having one functional group can be used, particularly when the curing agent has functionality greater than 2. All of the reactive diluent may be of functionality 2 or more, or the reactive diluent may comprise a mixture of a monofunctional compound with compounds of higher functionality.

The invention includes a curable acrylic polymer composition comprising an acrylic polymer of number average molecular weight  $M_n$  (determined by gas permeation chromatography (GPC)) less than 5000 containing pendant functional groups, dissolved in an organic compound of viscosity less than 20 poise at 25°C containing at least two

functional groups of the same functionality as that present in the acrylic polymer, and a curing agent which is reactive with the functional groups of the acrylic polymer and with the functional groups of the organic compound.

5       The invention is particularly useful in preparing curable acrylic polymer compositions which are epoxide-functional, that is comprising an epoxide-functional acrylic polymer (formed from a corresponding monomer) in a reactive diluent containing at least one epoxide group. An epoxide-  
10 functional acrylic monomer can for example be glycidyl acrylate or methacrylate.

Examples of ethylenically unsaturated comonomers which can be copolymerised with such a functional acrylic monomer are acrylic esters such as butyl acrylate or methacrylate,  
15 methyl methacrylate or acrylate, ethyl acrylate or methacrylate, propyl acrylate or methacrylate, n-hexyl acrylate or methacrylate, isopropyl acrylate or methacrylate, t-butyl acrylate or methacrylate, 2-ethyl-hexyl methacrylate or acrylate, cyclohexyl acrylate or  
20 methacrylate, 2,2,5-trimethylcyclohexyl acrylate or methacrylate, isobornyl acrylate or methacrylate, acrylonitrile, methacrylonitrile and vinyl compounds such as styrene, vinyl acetate or vinyl chloride.

The functional olefinically unsaturated monomer can  
25 alternatively be a vinyl or allyl monomer, for example the epoxide-functional monomer can be allyl glycidyl ether or vinyl-3,4-epoxycyclohexane. The monomers copolymerised with such a functional vinyl monomer can in general be any of those listed above, although vinyl monomers such as vinyl  
30 chloride and vinyl acetate may be preferred since acrylic monomers generally polymerise more readily and rapidly. If acrylic comonomers are used with a functional vinyl monomer care should be taken, for example by order of addition of monomers, to ensure that the functional vinyl monomer has  
35 been incorporated into the copolymer.

One preferred type of reactive diluent is a cyclic organic compound containing two alkyl groups each substituted by the functional group present in the functional acrylic or other olefinically unsaturated monomer. An epoxide-functional reactive diluent may for example be a cyclic compound substituted by at least two glycidyl groups. Examples of such compounds having the required viscosity include cyclohexanedimethanol diglycidyl ether, diglycidyl phthalate, diglycidyl cyclohexanedicarboxylate or resorcinol diglycidyl ether. Alternative epoxide-functional reactive diluents, preferably containing at least two glycidyl ether groups, which can be used in place of or together with the above include butanediol diglycidyl ether, pentaerythritol polyglycidyl ether, butyl glycidyl ether, octa-1,7-diene diepoxide, vinyl cyclohexene diepoxide and/or 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate.

The functional acrylic monomer and the ethylenically unsaturated comonomer(s), if used, are polymerised by addition polymerisation while in solution. The polymerisation is preferably carried out in the substantial absence of non-functional volatile solvent, that is solvent which will not react with the curing agent for the polymer. Alternatively a small proportion, for example up to 10 to 20% by weight of the polymerisation reaction mixture, of a non-functional volatile solvent which is miscible with the reactive diluent can be present. Some or all of the monomers can be pre-dissolved in the reactive diluent but preferably the monomers, together with the free radical initiator(s) and any chain transfer agent used, are gradually added to the diluent. For example, the reactive diluent can be heated to a temperature in the range 50-200°C, particularly 100-160°C, and the monomers, initiator and chain transfer agent are added over a period of up to 4 hours while maintaining the temperature of the solution during addition and for a further period of 0.5-4 hours after addition. A further charge of initiator may be added during this further period to reduce the level of unreacted monomer. The free radical

initiator can for example be a peroxide or peroxy-ester such as benzoyl peroxide or tertiary butyl peroctoate or an azo compound such as azobisisobutyronitrile or azo-bis(2-methylbutyronitrile).

5 A chain transfer agent, for example dodecanethiol, butanethiol, pentaerythritol tetra(mercaptopropionate) or dibutyl phosphite may be present during polymerisation. The level of initiator and of chain transfer agent, if present, are preferably controlled so that the number average  
10 molecular weight  $M_n$  of the polymer produced is no more than 10000 and is preferably in the range 600 to 5000, most preferably 1000 to 3000. For example, the amount of free radical initiator used (by weight based on monomers) is generally at least 1%, preferably 2 to 10%, when no chain  
15 transfer agent is used, or a level of 1 to 5% initiator can be used in conjunction with 1 to 10% chain transfer agent.

The curing agent which is present in the curable acrylic polymer composition can in general be any curing agent active in crosslinking the functional groups present  
20 in the acrylic polymer and in the reactive diluent under the intended conditions of curing. The curing agent for an epoxide-functional acrylic polymer composition can for example be thiol-functional or amino-functional. Most preferably the curing agent is a liquid polythiol of  
25 viscosity less than 20 poise at 25°C. Examples of such thiol-functional curing agents are pentaerythritol tetra(mercaptopropionate), trimethylolpropane tris(mercapto propionate) or a thiol-tipped low molecular weight polyether. Alternatively, the curing agent can be a liquid  
30 polyamine such as an aliphatic or aryl aliphatic diamine.

Alternative functional monomers are those which contain an activated - CH - group bonded to at least two electron-withdrawing groups, for example carbonyl, carboxyl, nitrile, nitro, phosphonate or phosphate ester groups. The activated  
35 - CH - group can for example be an acetoacetate group, a malonate ester group, a 1,3-diketone or a cyanoacetate.

group. A functional acrylic monomer can for example be an acetoacetatoalkyl methacrylate. Such an activated - CH - group-containing monomer can be polymerised with an ethylenically unsaturated comonomer of the type described 5 above. The reactive diluent to be used for the polymerisation generally contains at least one similarly activated - CH - group, for example an acetoacetate, malonate, 1,3-diketone or cyanoacetate group. It can for example be an acetoacetate ester, preferably an alkyl 10 acetoacetate such as ethyl acetoacetate, an acetoacetate ester of a polyol containing two or more acetoacetate groups such as ethylene glycol bis(acetoacetate) or 1,6-hexanediol bis(acetoacetate), acetylacetone or a dialkyl malonate such as dimethyl malonate. The polymerisation conditions are 15 generally as described above for epoxide-functional monomers.

The curing agent for an acrylic polymer composition having activated - CH - functionality is generally a material having at least two activated olefinic double 20 bonds, that is having a carboxyl, carbonyl or cyano group adjacent to the double bond. Curing takes place by Michael addition between the activated - CH - group and the activated double bond. Preferred curing agents are those containing alpha, beta-unsaturated carboxylic groups such as 25 acrylates. The curing agent for an activated - CH - functional composition can for example be a polyacrylate ester of a polyol such as trimethylolpropane triacrylate, trimethylolethane triacrylate, ethylene glycol diacrylate, 1,6-hexanediol diacrylate or pentaerythritol triacrylate or 30 tetraacrylate, or an acrylate-tipped oligomer such as a urethane acrylate, melamine acrylate, polyester acrylate, epoxy acrylate or silicone acrylate.

An alternative curing agent for an activated -CH- functionality is a polyamine containing at least two, 35 preferably at least three, primary or secondary amine groups.

The curing reaction between an activated -CH- group-functional polymer composition and a polyacrylate or a polyamine generally gives adequate cross-linking to form a hard solvent-resistant and weather-resistant coating even  
5 when the reactive diluent contains only one - CH - group, particularly when the curing agent contains at least three amine groups or activated double bonds such as trimethylolpropane triacrylate. The invention thus includes a curable acrylic polymer composition comprising an acrylic  
10 polymer of number average molecular weight less than 5000 having pendant groups each containing an activated - CH - group bonded to at least two electron-withdrawing groups, dissolved in a reactive diluent which is a liquid organic compound of viscosity less than 20 poise at 25°C containing  
15 at least one activated - CH - group bonded to at least two electron-withdrawing groups, and a curing agent which contains at least two activated C=C double bonds per molecule, said C=C bonds being activated by at least one vicinal electron-withdrawing group, or which contains at  
20 least two primary or secondary amine groups.

Another type of functional monomer which can be polymerised is an isocyanate-functional monomer such as isocyanatoethyl acrylate or methacrylate. This can be polymerised in a reactive diluent containing at least one,  
25 preferably at least two, isocyanate groups, such as toluene diisocyanate, hexamethylene diisocyanate, cyclohexylene diisocyanate or isophorone diisocyanate.

The curing agent for an isocyanato-functional acrylic polymer composition is an active hydrogen compound, for  
30 example a compound having at least two groups selected from hydroxyl and amino groups such as butanediol, trimethylolpropane and/or 2,4-diethyl-6-methyl-benzene-1,3-diamine.

Amines also undergo a crosslinking reaction with cyclic  
35 carbonates. A liquid cyclic carbonate such as propylene carbonate is a non-reactive solvent for isocyanate-

functional monomers and polymers and can be used as the solvent for the polymerisation of a monomer such as isocyanatoethyl methacrylate. The resulting composition can be cured by a polyamine which will react both with the  
5 isocyanate functionality of the acrylic polymer and with the propylene carbonate reactive diluent.

The functional acrylic monomer can alternatively be a hydroxy-functional acrylic monomer such as 2-hydroxyethyl acrylate or methacrylate. This can be polymerised in a  
10 reactive diluent containing at least two hydroxyl groups such as 1,2- or 1,4-cyclohexane-dimethanol. The resulting polymer composition can be cured with methylol-functional melamine resin.

If the curable acrylic polymer composition is intended  
15 to be cured at ambient temperature, it will generally be preferred that the curable acrylic polymer and reactive diluent are packaged separately from the curing agent and are mixed with it shortly before use. In the case of ambient curing coatings they can for example be mixed for up to 8  
20 hours, usually up to 2 hours, before application to a substrate or during application, for example in a twin-feed spray.

Another type of functional ethylenically unsaturated monomer which can be polymerised is an alkoxysilane-  
25 functional monomer such as 3-(trimethoxysilyl)-propyl acrylate or methacrylate or allyl triethoxy silane. This can be polymerised in a reactive diluent containing at least one, preferably at least two, alkoxy groups attached to silicon, such as phenyl methyl dimethoxy silane or methyl  
30 trimethoxy silane. The alkoxy groups attached to silicon are curable by moisture, so that care should preferably be taken to exclude moisture during the polymerisation and subsequent storage. The resulting polymer composition can be used as a single-pack moisture-curing coating composition.

35 The coating, sealant or adhesive composition may

contain additional ingredients. For example, a coating composition will generally contain one or more pigments, for example anticorrosive pigments such as zinc phosphate or sodium zinc molybdate, or colouring and opacifying pigments 5 such as titania, iron oxide or phthalocyanine pigments. A sealant composition will also generally contain pigments and/or fillers such as calcium carbonate or talc and all types of composition may contain additives such as plasticisers, thixotropes such as silica gel or bentonite 10 clay, or stabilising agents.

The invention is illustrated by the following Examples:-

Example 1

<u>Formulation</u>	<u>Weight in grams</u>
15 3,4-epoxycyclohexylmethyl 3,4-epoxy-cyclohexane carboxylate	250
Methyl Methacrylate	48.1
Butyl Acrylate	252.4
Glycidyl Methacrylate	144.2
20 Dodecanethiol (chain transfer agent)	38.9
3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate	50
t-Butyl Peroctoate (initiator)	17.6

Procedure

25 250g 3,4-epoxycyclohexylmethyl 3,4-epoxy-cyclohexane carboxylate was charged to a vessel fitted with condenser, N<sub>2</sub> purge, stirrer thermometer and addition port and heated to 150°C under N<sub>2</sub>. The monomers and dodecanethiol and the initiator in 50g 3,4-epoxycyclohexyl 3,4- 30 epoxycyclohexanecarboxylate were separately charged to the heated vessel over 2 hours and held at 150°C for 1 hour more. An initiator boost of 1g was added and the vessel was

held at 150°C for a further hour.

The resulting polymer composition had a viscosity of 26.2 poise as measured by cone and plate viscometer at 25°C, a measured epoxy equivalent weight of 245 and a measured non-volatile content (1 hour at 150°C) of 94.9% by weight. The number average molecular weight  $M_n$  was 1266 and the weight average molecular weight  $M_w$  was 2280, as measured by GPC.

The stripped composition was mixed with a stoichiometric equivalent amount of pentaerythritol tetramercaptopropionate, which reduced the viscosity to below 10 poise, and was sprayed on a steel panel and allowed to cure to a clear tough coating at ambient temperature.

#### Example 2

##### 15 Formulation

	<u>% by Weight</u>
1. Ethyl Acetoacetate	26.13
2. Styrene	26.17
3. Acetoacetoxyethyl Methacrylate	32.35
4. Methyl Methacrylate	7.21
20 5. 2,2'-Azobis-(2-methylbutyronitrile) (initiator)	1.41
6. 2-Mercaptoethanol	2.78
7. Initiator	0.08
8. Ethyl Acetoacetate	3.87

1 was charged to a reaction vessel and heated to 100°C. 2, 25 3, 4, 5, 6 were mixed together and added to 1 in the reaction vessel over 4 hours, maintaining the temperature of 100°C, and held at 100°C for 30 minutes more. 7 and 8 were mixed and added to the reaction vessel, which was held for a further 1 hour at 100°C. The polymer solution produced had 30 viscosity 15 poise,  $M_n$  1800 and  $M_w$  3100 relative to polystyrene by GPC.

100g of polymer solution was mixed with 57.2g of trimethylolpropane triacrylate and 1.26g of diazabicycloundecene catalyst (as a 10% w/w solution in

methoxypropyl acetate). The resulting composition was sprayed as a coating and allowed to cure to give a film with hardness 80 Konig swings after 7 days' cure at ambient temperature.

5

Example 3

<u>Formulation</u>	<u>Weight in grams</u>
Cyclohexane Dimethanol	300
Butyl Acrylate	252.4
Hydroxy Ethyl Acrylate	117.7
10 Methyl Methacrylate	48.1
Dodecanethiol	38.9
Xylene	50
t-Butyl Peroctoate	17.6

The above formulation was polymerised using the procedure of Example 1 to form a polymer solution having a non-volatile content of 83.7%, a viscosity of 32 poise and a hydroxyl value of 329. The polymer had  $M_n$  1050 and  $M_w$  1770.

The polymer solution was used as the basis of a coating composition cured by a "Cymel" methoxymethyl melamine resin.

Example 4

<u>Formulation</u>	<u>Weight in grams</u>
Cyclohexanedimethanol diglycidyl ether	1000.0
Butyl Acrylate	1009.6
25 Glycidyl Methacrylate	849.2
Dodecanethiol	311.2
Cyclohexanedimethanol diglycidyl ether	300.0
t-Butyl peroctoate	70.4
	<hr/>
30	3444.4
	<hr/>

The above formulation was polymerised using the procedure of Example 1 to form a polymer solution of viscosity 6 poise, non-volatile content 90.5% and epoxy equivalent weight 263.

A coating composition was prepared using the same curing agent as in Example 1 and had viscosity 5.4 poise. It was sprayed and cured at ambient temperature and was dry to handle after 1.5 hours. When cured at 5°C the coating was 5 dry to handle within 18 hours.

Example 5

<u>Formulation</u>	<u>Weight in grams</u>
Cyclohexanedimethanol diglycidyl ether	150.0
Glycidyl methacrylate	262.6
10 Dodecanethiol	37.4
Cyclohexanedimethanol diglycidyl ether	50.0
t-Butyl peroctoate	7.9

The above formulation was polymerised using the procedure of Example 1 to form a polymer solution of 15 viscosity 24.5 poise, non-volatile content 91.1% and epoxy equivalent weight 168.5.

When mixed with a stoichiometric amount of the curing agent of Example 1, a sprayable coating composition was formed.

20

Example 6

<u>Formulation</u>	<u>Weight in grams</u>
Cyclohexanedimethanol diglycidyl ether	156
Butyl Acrylate	157
Glycidyl methacrylate	132
25 Dibutyl Phosphite	28
Cyclohexanedimethanol diglycidyl ether	31
t-Butyl peroctoate	11

The above formulation was polymerised using the procedure of Example 1 to form a polymer solution of 30 viscosity 28 poise, non-volatile content 91.8% and epoxy equivalent weight 244.5.

A paint base was prepared by milling the following in a high speed disperser to below 40 microns.

Polymer solution prepared above	300 g
Structuring agents (modified clays)	30 g
Titanium dioxide	931 g

and diluting the milled product with 771 g more of the  
5 polymer solution.

1940g of the resulting paint base was mixed with 5.2 g  
acrylic polymer flow aid, 572 g pentaerythritol tetra  
(mercaptopropionate) and 48.5 g dimethyl 1010 amine as an  
auxiliary curing agent to form a white paint of pot life  
10 over 30 minutes. The paint was sprayed on steel panels at a  
film thickness of 200 microns and was allowed to cure at  
ambient temperature (about 25°C). The paint film was through  
dry (hard enough to handle) after 2 hours.

#### Example 7

<u>15 Formulation</u>	<u>Weight in grams</u>
Phenylmethyldimethoxysilane	190.0
Butyl acrylate	246.5
3-(Trimethoxysilyl)-propyl methacrylate	85.0
3-Mercapto propyl trimethoxysilane	28.5
20 Phenylmethyldimethoxysilane	50.0
Azo-bis(2-methyl-butyronitrile)	13.1
	<hr/>
	613.1

25 The above formulation was polymerised using the  
procedure of Example 2 to form a polymer solution suitable  
for use as a coating composition.

The polymer solution was sprayed on a steel panel and  
allowed to cure by moisture under atmospheric conditions to  
30 form a clear hard coating.

CLAIMS

1. A process for the preparation of a curable polymer composition by the free radical polymerisation of a functional olefinically unsaturated monomer, which contains  
5 a functional group which is capable of reacting with a curing agent, and optionally one or more ethylenically unsaturated comonomers, characterised in that the polymerisation is carried out in the presence of a reactive diluent which is a liquid organic compound of viscosity less  
10 than 20 poise at 25°C having at least one functional group which is substantially non-reactive with the functional olefinically unsaturated monomer and which is capable of reacting with a curing agent to form a polymer network.

2. A process according to claim 1, characterised in  
15 that the functional group of the reactive diluent is capable of reacting with the same curing agent with which the functional group of the monomer reacts, so that the curable polymer and the reactive diluent can be linked by the curing agent in the same polymer network.

20 3. A process according to claim 1 or claim 2, characterised in that the monomer is an acrylic ester substituted by a reactive functional group.

4. A process according to any of claims 1 to 3, characterised in that the reactive diluent contains at least  
25 two of the said functional groups per molecule.

5. A process according to claim 4, characterised in that the reactive diluent is a cyclic organic compound containing two alkyl groups each substituted by the said functional group.

30 6. A process according to any of claims 1 to 5, characterised in that the functional group of the reactive diluent has the same functionality as the functional olefinically unsaturated monomer.

7. A process according to claim 6, characterised in that the functional monomer is an epoxide-functional acrylic monomer and the reactive diluent contains at least one epoxide group.

5 8. A process according to claim 7, characterised in that the functional acrylic monomer is glycidyl acrylate or methacrylate.

9. A process according to claim 7 or claim 8, characterised in that the reactive diluent contains at least  
10 two glycidyl groups.

10. A process according to any of claims 1 to 6, characterised in that the functional monomer contains an activated - CH - group bonded to at least two electron-withdrawing groups and the reactive diluent contains at  
15 least one activated - CH - group bonded to at least two electron-withdrawing groups.

11. A process according to claim 10, characterised in that the functional monomer is an acetoacetatoalkyl methacrylate.

20 12. A process according to claim 10 or claim 11, characterised in that the reactive diluent is an acetoacetate ester.

13. A process according to any of claims 1 to 6, characterised in that the functional monomer is an  
25 isocyanate-functional monomer and the reactive diluent contains at least one isocyanate or cyclic carbonate group.

14. A process according to any of claims 1 to 13, characterised in that the polymerisation is carried out in the substantial absence of non-functional volatile solvent.

30 15. A curable addition polymer coating composition of viscosity 1 to 10 poise, characterised in that the

composition is prepared by a process according to any of claims 1 to 14.

16. A process for coating a substrate with a curable addition polymer composition, characterised in that a 5 curable polymer composition prepared according to any of claims 1 to 11 is applied to the substrate without dilution by a volatile organic solvent.

17. A curable acrylic polymer composition comprising an acrylic polymer of number average molecular weight less 10 than 5000 containing pendant epoxide functional groups, dissolved in an organic compound of viscosity less than 20 poise at 25°C containing at least one epoxide group, and a curing agent which is reactive with epoxide groups.

18. A curable acrylic polymer composition according to 15 claim 17, characterised in that the said organic compound is a cyclic compound substituted by at least two glycidyl groups.

19. A curable acrylic polymer composition according to claim 18, characterised in that the said organic compound is 20 selected from cyclohexanedimethanol diglycidyl ether, diglycidyl phthalate, diglycidyl cyclohexanedicarboxylate and resorcinol diglycidyl ether.

20. A curable acrylic polymer composition according to any of claims 17 to 19, characterised in that the curing 25 agent is a liquid polythiol of viscosity less than 20 poise at 25°C.

21. A curable acrylic polymer composition comprising an acrylic polymer of number average molecular weight less than 5000 having pendant groups each containing an activated 30 - CH - group bonded to at least two electron-withdrawing groups, dissolved in a reactive diluent which is a liquid organic compound of viscosity less than 20 poise at 25°C containing at least one activated - CH - group bonded to at

least two electron-withdrawing groups, and a curing agent which contains at least two activated C=C double bonds per molecule, said C=C bonds being activated by at least one vicinal electron-withdrawing group, or which contains at least two primary or secondary amine groups.

22. A curable acrylic polymer composition according to claim 21, characterised in that the acrylic polymer has pendant acetoacetate groups.

23. A curable acrylic polymer composition according to claim 21 or claim 22, characterised in that the reactive diluent is an acetoacetate ester.

24. A curable acrylic polymer composition according to any of claims 21 to 23, characterised in that the curing agent is a polyacrylate ester of a polyol.

25. A curable acrylic polymer composition comprising an acrylic polymer of number average molecular weight less than 5000 containing pendant functional groups dissolved in an organic compound of viscosity less than 20 poise at 25°C containing at least two functional groups of the same functionality as that present in the acrylic polymer, and a curing agent which is reactive with the functional groups of the acrylic polymer and with the functional groups of the organic compound.

26. A curable acrylic polymer composition according to any of claims 17 to 25, characterised in that the composition is a coating composition which is substantially free of non-reactive volatile solvent and has a viscosity of 1 to 20 poise at 25°C.



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Claims searched: 1-26

Examiner: Alan Kerry  
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**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK Cl (Ed.O): C3P PJL  
Int Cl (Ed.6): C08F 2/06, 2/08, 2/14  
Other: Online databases: WPI, CLAIMS

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2243368 A (SHERWIN-WILLIAMS) see Claims 9,10 and Examples 4-8	1-4, 6, 25
X	US 4652605 (PPG) see Claims 1, 3, 6-8; Examples I-VI	1-4, 6, 25
X	US 4629764 (DOW) see Claims 1, 6; Examples 1-5	1-6, 25

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

